



Effect of Al_2O_3 and CaF_2 additives on the viscosity of conventional cryolite melts

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Abstract

The viscosity of cryolite melts of conventional composition $\text{NaF-AlF}_3\text{-CaF}_2\text{-Al}_2\text{O}_3$ was studied by rotational viscometry using the FRS 1600 high-temperature rheometer. The cryolite ratio of the NaF-AlF_3 melt was 2.1, 2.3, and 2.5; the Al_2O_3 content varied from 2 to 6.6, and CaF_2 – from 0 to 8 wt%. The measurements were carried out in the temperature range from liquidus to 1200 °C. The conditions for the laminar flow of the investigated melts were determined, based on the measurements of the cryolite melts viscosity as a function of the shear rate at a constant temperature. A shear rate of $12 \pm 1 \text{ s}^{-1}$ was chosen for studying the viscosity temperature dependence for all samples. The viscosity temperature dependence of cryolite melts is described by a linear equation. The temperature coefficient b in this equation has negative values and varies in the range of $(-0.01)\text{--}(-0.06) \text{ mPa}\cdot\text{s}/\text{deg}$. It was found that the viscosity of cryolite melts of conventional composition in the range of operating temperatures of aluminum electrolysis (950–970 °C) varies from 2.5 to 3.7 mPa·s (depending on the composition and temperature). The viscosity of cryolite-alumina melts increases with the rise of alumina content: 1 wt% Al_2O_3 increases the viscosity, on average, by 1%. However, the influence of CaF_2 is more significant: the addition of 1 wt% CaF_2 leads to an increase in viscosity by 3%. A decrease in the CR of the melt by 0.1 (in the range of 2.1–2.5) leads to a decrease in the viscosity of cryolite melts by 2.3%. A viscosity regression equation for the cryolite melts of conventional composition as a function of several independent parameters (temperature, CR, CaF_2 and Al_2O_3 content) is obtained by the multivariable approximation of experimental data. The equation satisfactorily (within 1.5%) describes the viscosity of conventional industrial electrolytes and can be used for estimation of their viscosity.

Keywords

molten cryolite
alumina
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rotary method

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1. Introduction

According to the International Aluminum Institute, the worldwide aluminum production amounted 65.296 million tons in 2020, of which 3.72 million tons were produced in Russia. Nonetheless, the classic Hall–Héroult process for producing aluminum is more than 140 years old. It is comprised on the electrolysis of dissolved aluminum oxide (alumina) in molten cryolite. The melting point of alumina is 2044 °C, therefore, in order to obtain primary alumi-

num, the alumina has to be dissolved in sodium cryolite, whereas electrolysis is carried out at 950–970 °C.

The conventional electrolyte is composed on the base of sodium cryolite (Na_3AlF_6), besides the additions of AlF_3 , CaF_2 , MgF_2 are added [1]. These electrolytes possess a high solubility of alumina [2]. The electrolyte is characterized by such parameter as the cryolite ratio (CR), expressed by the molar ratio of sodium fluoride to aluminum fluoride. The sodium cryolite has the $\text{CR} = 3$, and the CR of industrial electrolytes can vary from 2.1 to 2.7 [3].

One of the main parameters defining the electrolysis process is the current efficiency. The current efficiency during electrolysis is influenced by many factors: process temperature, pole-to-pole distance, current density, composition and physicochemical properties of the electrolyte, cell design, etc. One of the most important characteristics of molten cryolite-alumina electrolytes, which determine the processes of mass and heat transfer in an aluminum cell, is viscosity. It also determines the following hydrodynamic processes: electrolyte circulation, rate of alumina dissolution, flotation and sedimentation of alumina particles, transfer of dissolved and undissolved alumina in the electrolyte bulk, transfer and release of anode gas, nature of chemical and electrode reactions [4, 5].

Nowadays, the most reliable and systematic data related to the viscosity of cryolite melts is considered to be the results obtained by Torklep and Oye in 1980 [6]. They measured the viscosity of cryolite melts in wide ranges of CR (the AlF_3 content was varied from 5 to 35 mol.%) and temperature by an oscillation method. The viscosity of cryolite melts depending on CR was obtained to be non-linear. The maximum value (~ 2.3 mPa/s at 1000 °C) accumulated in the melt with CR = 4. Abnormal behavior of melts with low CR was detected (random movements of the pendulum, very large differences between periodic viscosity and damping viscosity, irreproducibility of results, etc.). The authors suggest that one of the several possible reasons for the observed behavior of acidic melts is insufficient mixing. In the region of high CRs, the difficulties in dissolving of oxide were noted. It was the reason for the increase in the duration of experiments in order to obtain completely reproducible values. The viscosity measurements were carried out from high temperature in every 10–20 degrees, lowering temperature to the expected liquidus point. The frequent overcooling of the cryolite-alumina melts was observed, which led to the fact that measurements of some compositions were conducted in the two-phase region. In cryolite-alumina melts with the Al_2O_3 content up to 4 wt%, the viscosity temperature dependences were almost parallel to the curves obtained in the NaF-AlF_3 binary system, especially for melts with low CR. The inflection point on the binary curve become even more pronounced with an increase in the Al_2O_3 content.

Authors [6, 7, 8] measured the viscosity of the $\text{NaF-AlF}_3\text{-Al}_2\text{O}_3$ ternary system depending on CR and Al_2O_3 concentration. It should be noted that some experimental results were presented at temperatures below the liquidus of the corresponding mixtures. This may explain why the measured viscosities of these two-phase samples (consisting of a suspension of some solid particles of aluminum oxide and corundum in the liquid phase) are significantly higher than the calculated viscosities of "hypothetical" liquid (single-phase) samples. In this case, no bends are observed on the curves.

The viscosity of cryolite melts containing CaF_2 were described in articles [8, 9]. The viscosity values obtained by different authors differ significantly. Moreover, the comparison of viscosity values is often difficult due to the significantly different multicomponent mixtures of cryolite melts.

Researchers [5] determined the temperature dependences of density, viscosity, surface and interfacial tension in a system with low CR: 55 mol.% NaF + 45 mol.% AlF_3 . The viscosity was measured in the temperature range from 725 to 840 °C, and a quadratic equation for the viscosity temperature dependence was obtained for the cryolite melts of eutectic composition (CR = 1.22).

In paper [10] a thermodynamic model was suggested for calculating the viscosity of multicomponent fluoride systems. The authors used the thermochemical program FactSage [11].

Thus, despite the importance of viscosity for the technological process, the viscosity of cryolite melts of conventional electrolytes has not been properly studied yet. According to various authors, the viscosity of the conventional electrolyte $\text{NaF-AlF}_3\text{-CaF}_2\text{-Al}_2\text{O}_3$ in the CR range from 1.8 to 2.6 and 945–970 °C varies in the range from 1 to 5 mPa·s [10, 12].

The limited number of studies related to the viscosity of cryolite melts can be explained by the great experimental difficulties associated with the choice of structural materials, due to the aggressiveness of fluoride melts and high measurement temperatures (about 1000 °C), as well as with rather low values of the molten salts viscosity.

The purpose of this work was to study the effect of temperature, cryolite ratio, CaF_2 and Al_2O_3 content on the viscosity of cryolite melts of the conventional composition $\text{NaF-AlF}_3\text{-CaF}_2\text{-Al}_2\text{O}_3$ with the CR = 2.1–2.5 in a wide temperature range using the rotational viscometry; the focus was also set on the obtaining of the viscosity multiparameter regression equation for the molten conventional electrolytes.

2. Experimental

2.1. Composition and preparation of melts

Molten mixtures were prepared from individual substances NaF (specifically pure grade), AlF_3 (highly pure grade), and CaF_2 (pure grade) (Vekton).

A weighed amount of components was loaded into a glassy carbon crucible and remelted at 990 °C for 2 hours in a shaft furnace. The prepared mixtures were stored in a closed container.

The compositions of the studied samples are presented in Table 1.

2.2. Rotational viscometry method

A liquid is placed in a small gap, necessary for the shear of the medium, between two cylinders: an inner cylinder with a radius R_o and an outer one with a radius R_i .

Table 1 Composition of cryolite melts

CR	NaF		AlF ₃		CaF ₂ , wt%	Al ₂ O ₃ , wt%
	wt%	mol.%	wt%	mol.%		
2.1	48.7	65.3	46.3	31.1	0	3.0
					5.0	3.0
					5.0	6.5
					8.0	6.5
2.3	50.8	67.2	44.2	29.2	0	2.0
					5.0	2.0
					5.0	4.0
					0	2.0
2.5	52.8	68.9	42.2	27.6	5.0	2.0
					5.0	4.0
					5.0	6.0
					5.0	6.0

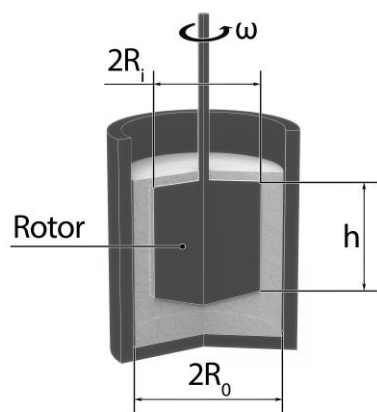
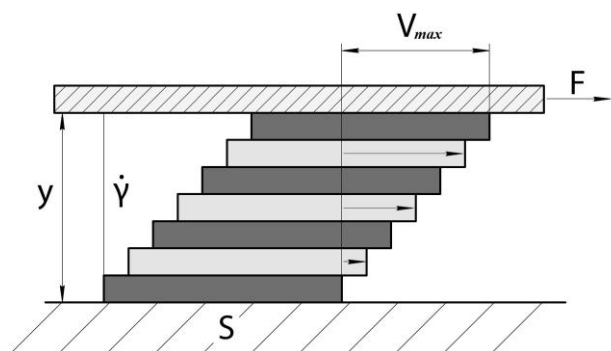
A schematic diagram of a rotating cylindrical viscometer is shown in Fig. 1.

During measurements, the outer cylinder rotates at a constant rate, while the inner cylinder is given a rotational torque, which is a measure of viscosity. The viscosity (η) is calculated by the following equation:

$$\eta = \frac{1}{\omega} \left(\frac{M}{4\pi h} \right) \left(\frac{1}{R_i^2} - \frac{1}{R_o^2} \right) = k \frac{M}{\omega} \quad (1)$$

where M is the torque acting on the cylindrical surface, N·m; ω is the angular velocity, rad/s; h is the depth of immersion of the inner cylinder in a liquid medium, m; R_i is the radius of the inner cylinder, m; R_o is the radius of the outer cylinder, m; k – is the constant of the device, rad/m³.

The parallel plane model, schematically depicted in Fig. 2, helps defining both shear stress (τ) and shear rate ($\dot{\gamma}$) [13].

**Fig. 1** Schematic diagram of a cylindrical viscometer**Fig. 2** The flow between two parallel planes

The force F , applied to the area S located at the interface between the upper plane and the fluid below it, causes a flow in the fluid layer:

$$\tau = \frac{F}{S} \quad (2)$$

where τ is the shear stress, Pa (N/m²); F is the force applied to the area S , N; S is the area, m².

The shear stress produces a characteristic pattern of layer-by-layer rate distribution in the fluid layer. The maximum flow rate V_{max} is observed at the interface between the liquid and the moving plane [13].

The flow rate decreases with the distance from the moving plane, and at a distance y from it, at the boundary with the fixed plane, $V_{min} = 0$. The laminar flow means that the liquid layers of infinitesimal thickness slide over one another. One laminar layer is displaced relative to the other by some part of the total shear of the entire liquid layer between both planes. The velocity gradient across the gap is called the shear rate, which is mathematically expressed as a differential:

$$\dot{\gamma} = \frac{dv}{dy}, \quad \left[\frac{\text{m/s}}{\text{m}} = \text{s}^{-1} \right]. \quad (3)$$

The dynamic viscosity is defined as

$$\eta = \frac{\tau}{\dot{\gamma}}, \quad \left[\frac{\text{N/m}^2}{\text{s}^{-1}} = \text{Pa} \cdot \text{s} \right]. \quad (4)$$

2.3. Measurement techniques

The viscosity measurements of the cryolite melts with different CR and additive concentrations were carried out using an FRS 1600 rheometer, the principle of operation of which is based on the rotary method.

The studied sample is placed in an outer graphite cylinder (Fig. 3). The inner cylinder slowly immerses and rests against the solid sample with a force of 3 N, after which the furnace starts heating. After reaching the liquidus temperature, the rotor begins rotating at a low rate in order to homogenize the melt. The fact that the sample has passed into a single-phase state can be judged by the steady-state values of the viscosity. The viscosity measurements can be performed either at a constant temperature or according to a given program for cooling the melt in a dynamic mode.

3. Results and discussion

3.1. Selecting the "shear rate" parameter

In order to obtain the correct viscosity values, a laminar flow has to be established in the sample. This means that it takes time for the substance to start moving at a rate corresponding to the applied shear stress.

In order to determine the conditions for the laminar flow the viscosity of all cryolite samples was measured as a function of the shear rate at a constant temperature. As

an example, the dependence of the viscosity of cryolite samples with the CR = 2.5 on the shear rate in logarithmic coordinates is presented in Fig 4. The shear rate varies from 2 to 50 s⁻¹.

It is seen in the Fig. 4 that at low shear rate (up to 10 s⁻¹), a large scatter of points is observed, which is due to the fact that the laminar flow was not established yet. The laminar flow is realized when the viscosity does not depend on the shear rate, that is, in the horizontal section in the shear rate range of 10–16 s⁻¹. With an increase in the shear rate above 16 s⁻¹, the viscosity rises sharply, which is associated with incipient turbulence.

In order to study the temperature dependence of the viscosity of all samples, a shear rate of 12 ± 1 s⁻¹ was chosen.

3.2. The viscosity temperature dependence of the cryolite melts

The viscosity measurements were started at 1020 °C, then the temperature was decreased to a temperature few degrees above liquidus. The cooling rate was 2 °C/ min. The liquidus temperature was calculated using the equation given in [14]. The calculated values of the liquidus temperature are listed in Table 2.

The viscosity temperature dependence of the cryolite melts with the CR = 2.1 is given in Fig. 5.

The viscosity temperature dependence of all samples in the temperature range from the liquidus to 1200 °C is described by a linear equation of the type:

$$\eta = a + bT \quad (5)$$

where a and b are experimental constants.

The equations for the viscosity temperature dependence of the cryolite melts are summarized in Table 2. For all equations, the coefficient of determination R^2 has a value of at least 0.97. The viscosity of the cryolite samples at the operating temperatures of aluminum electrolysis 950 and 970 °C are given in Table 2.

As the temperature rises the viscosity of the molten salt decreases.



Fig. 3 Internal and external cylinders and the shaft furnace Carbolite STF16/180

The temperature coefficient b in equation (5) has negative values and varies in the range of (–0.01)–(–0.06) mPa·s/deg for all tested samples. Thus, the change in temperature has a decisive influence on the change in the viscosity of the electrolyte.

3.3. Effect of CR, CaF₂ and Al₂O₃ content

The viscosity temperature dependence of the cryolite-alumina melts with different CR is shown in Fig. 6. The figure also demonstrates the literature data [6] and [15] on the viscosity of melts, which are the closest to ours in composition and temperature range of measurements.

The data diverge quite significantly, although the temperature coefficients are close. It should be noted that due to the complex multicomponent compositions of electrolytes for aluminum production, it is difficult to find completely identical compositions in the references, and no generalizing equations have been found. Moreover, the results of works [6] and [15] were obtained by the oscillation method, the disadvantages of which were described above. In addition, data on the density were used to calculate the dynamic viscosity of these compositions, which introduces an additional error in the result.

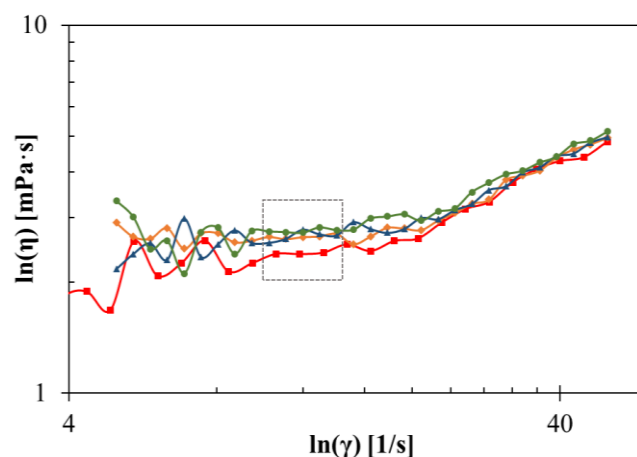


Fig. 4 The viscosity of cryolite melts with the CR = 2.5 depending on the shear rate at 1020 °C: ■ – without additives; ◆ – 5 wt% CaF₂; ▲ – 5 wt% CaF₂ and 2 wt% Al₂O₃; ● – 5 wt% CaF₂ and 2 wt% Al₂O₃

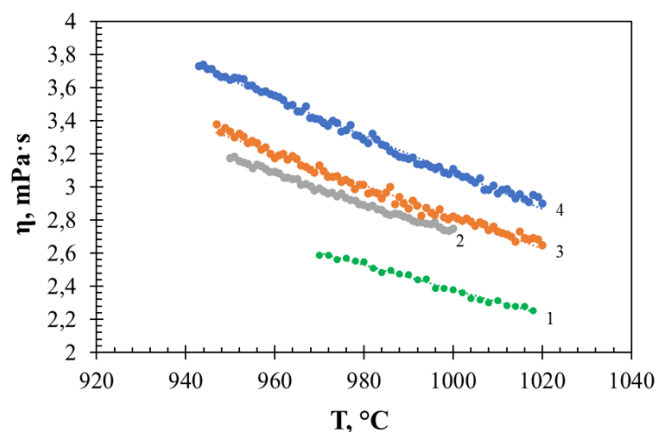


Fig. 5 The viscosity temperature dependence of the cryolite melts with CR = 2.1 and different content of CaF₂ and Al₂O₃ (wt%): 1 – 0 CaF₂ + 3 Al₂O₃; 2 – 5 CaF₂ + 3 Al₂O₃; 3 – 5 CaF₂ + 6.5 Al₂O₃; 4 – 8 CaF₂ + 6.5 Al₂O₃

Table 2 Viscosity (mPa·s) of the cryolite melts of conventional composition

Nº	CR	CaF ₂ , wt%	Al ₂ O ₃ , wt%	<i>a</i>	<i>b</i>	<i>R</i> ²	η (950 °C)	η (970 °C)	<i>T</i> _{liq} [14]
1	2.1	0	3.0	9.837	-0.0075	0.985	-	2.56	958
2		5.0	3.0	11.716	-0.009	0.99	3.17	2.99	940
3		5.0	6.5	12.37	-0.0096	0.98	3.25	3.06	931
4		8.0	6.5	14.234	-0.0111	0.99	3.67	3.46	920
5	2.3	0	2.0	10.023	-0.0075	0.97	-	2.67 (980 °C)	975
6		5.0	2.0	9.011	-0.0063	0.97	-	2.90	960
7		5.0	4.0	9.832	-0.007	0.98	3.18	3.04	949
8	2.5	0	2.0	9.506	-0.0069	0.75	-	-	990
9		5.0	2.0	9.9867	-0.0072	0.93	-	-	978
10		5.0	4.0	10.168	-0.0073	0.96	-	2.97 (980 °C)	965
11		5.0	6.0	10.438	-0.0075	0.97	-	3.115	958

According to our data, the CR alteration by 0.1 changes the viscosity of cryolite-alumina melts in average by 0.1 mPa·s, which is 2.3%. The viscosity of cryolite melts in the temperature range of 950-970 °C varies from 2.5 to 3.7 mPa·s (depending on the composition).

It can be concluded, based on the results presented in Table 2, that both the CaF₂ and Al₂O₃ additives effect the cryolite melts viscosity.

The viscosity of cryolite-alumina melts rises with increasing alumina content. The addition of 1 wt% Al₂O₃ increases by 1% the viscosity of conventional electrolyte, on average.

Calcium fluoride significantly increases the viscosity of cryolite-alumina melts. The addition of 1 wt% CaF₂, on average, increases the electrolyte viscosity by 3%. Considering that CaF₂ impacts the thermal conductivity of cryolite melts, and acts as a part of the side ledge of the electrolysis bath, that is, plays an important role in the thermal balance of an aluminum cell, its concentration in conventional electrolyte is an important value and requires special control.

3.4. Multiparameter equation of the viscosity

The general regression equation for the dependence of the conventional cryolite electrolyte viscosity on several parameters was derived by the multivariable data approximation. The data set included the following parameters: temperature, cryolite ratio, calcium fluoride and alumina content. The resulting equation for the viscosity of cryolite melts is the following:

$$\eta = 71.75 - 0.133 \cdot T - 8.21 \cdot 10^{-3} \cdot C(\text{Al}_2\text{O}_3) + 0.333 \cdot \text{CR} + 0.0796 \cdot C(\text{CaF}_2) - 0.625 \cdot 10^{-5} \cdot T^2 - 2.08 \cdot \left(\frac{C(\text{CaF}_2) + C(\text{Al}_2\text{O}_3)}{C(\text{Al}_2\text{O}_3)} \right)^{1.5} + 8.12 \cdot 10^{-5} \cdot C(\text{Al}_2\text{O}_3)^3; \quad (6)$$

$$R^2 = 0.99$$

where *T* is temperature, °C; *C*(Al₂O₃) and *C*(CaF₂) are the content of components, wt%; CR is the cryolite ratio.

The equation is valid within the temperature range from liquidus to 1020 °C at CR 2.1–2.5, the CaF₂ content 0–8 wt%, the Al₂O₃ content 2–6.5 wt%.

The equation is valid in the temperature range from liquidus temperature to 1020 °C, in the concentration ranges of CR 2.1–2.5, alumina from 2 to 6.5 wt%, and calcium fluoride from 0 to 8 wt%.

A comparison of the experimental and calculated by equation (6) viscosity data for the cryolite melt with CR = 2.3 is shown in Fig. 7.

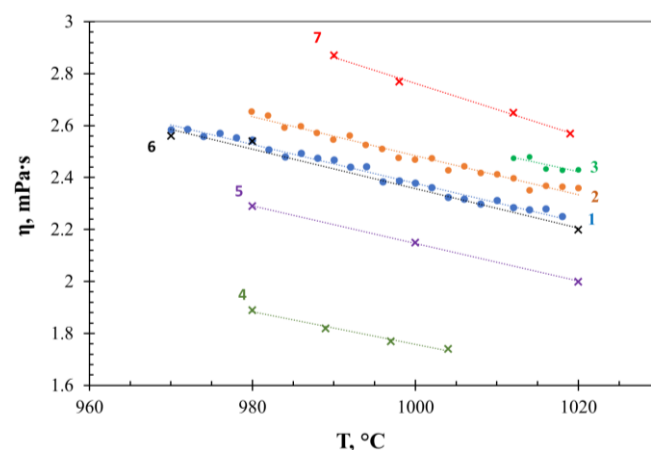


Fig. 6 The viscosity temperature dependence of the NaF-AlF₃ melt with different CR and Al₂O₃ content (wt%): 1 – CR = 2.1, Al₂O₃ = 3; 2 – CR = 2.3, Al₂O₃ = 4; 3 – CR = 2.5, Al₂O₃ = 2; 4 – CR = 2.1 [15]; 5 – CR = 2.3, Al₂O₃ = 4 [6]; 6 – CR = 2.3, Al₂O₃ = 8 [6]; 7 – CR = 2.3, Al₂O₃ = 12 [6]

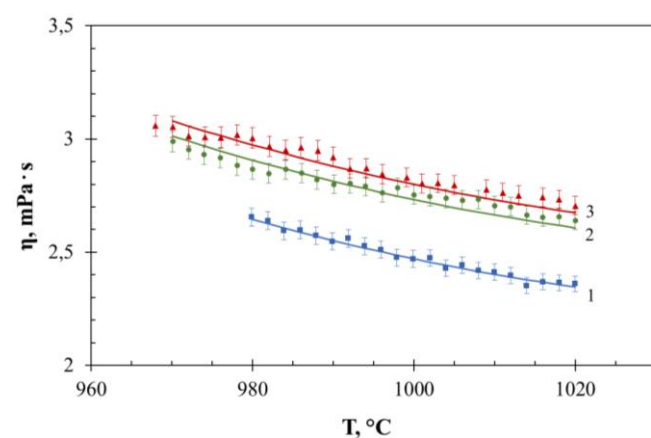


Fig. 7 Experimental and calculated viscosity for cryolite melts with CR = 2.3. Concentration of additives – in wt%: 1 – CaF₂ = 0, Al₂O₃ = 2; 2 – CaF₂ = 5, Al₂O₃ = 2; 3 – CaF₂ = 5, Al₂O₃ = 4; points – experiment, lines – calculation

The calculated viscosity is given as solid lines in Fig. 4 and the experimental data – as dots. The experimental and calculated values of the viscosity of conventional cryolite electrolyte coincide within 1.5%.

Conclusions

The viscosity of the conventional cryolite melts $\text{NaF-AlF}_3\text{-CaF}_2\text{-Al}_2\text{O}_3$ in the temperature range of 950–970 °C varies from 2.5 to 3.7 mPa·s (depending on the composition). The viscosity increases with the rise in the content of additives: per addition of 1 wt% Al_2O_3 the viscosity, on average, increases by 1%, while the addition of 1 wt% CaF_2 increases the melt viscosity by 3%. A decrease in the CR of the melt by 0.1 results in a viscosity decrease (in the range of the CR 2.1–2.5) by 2.3%.

The regression equation for estimating viscosity of cryolite melts on several independent parameters, obtained by approximating the experimental data, satisfactorily describes (within 1.5%) the viscosity of conventional electrolytes for aluminum production.

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